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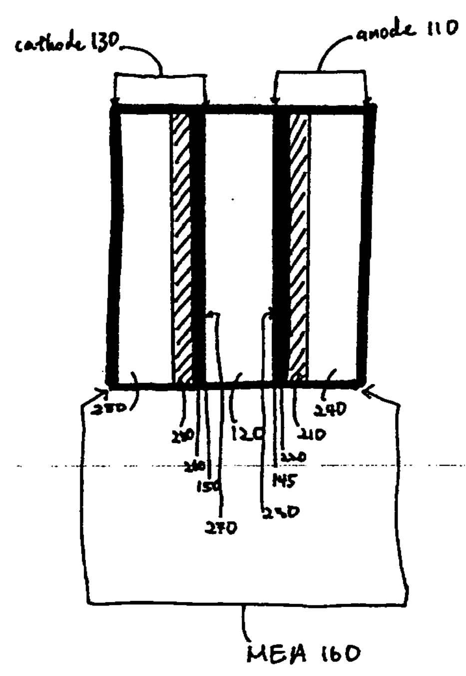
(54) Title: ASYMMETRIC ELECTRODES FOR DIRECT-FEED FUEL CELLS

(57) Abstract

An improved direct-feed fuel cell having a solid membrane electrolyte (120) for electrochemical reactions of an organic fuel. Fuel crossover has been reduced due to pore structures blockage at the electrode-membrane interfaces (230, 270) of the membrane electrode assembly (160). Two improved MEA's are disclosed. One utilizes a multi-layer catalyst formation with a densest catalyst layer (220, 260) applied at the electrode-catalyst interfaces (230, 270). Another utilizes an inert pore blocking layer (320, 340) at the electrode-membrane interfaces (230, 270).



Multi-layer Catalyst Application

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Asymmetric Electrodes for Direct-Feed Fuel Cells

Origin of Invention

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

Field

This disclosure generally relates to organic fuel cells for use in the generation of electrical energy and in particular liquid direct-feed organic fuel cells and the manufacturing thereof.

Background

Fuel cells are electrochemical cells in which a free energy change resulting from a fuel oxidation reaction is converted into electrical energy. Fuel cells use renewable fuels such as methanol; typical products from the electrochemical reactions include carbon dioxide and water. Fuel cells may be an attractive alternative to the combustion of fossil fuels.

Previously, fuel cells used reformers to convert methanol into hydrogen gas for use by fuel cells. Direct oxidation fuel cells can offer weight and volume advantage over the indirect reformer fuel cells. However, initial direct oxidation models used a strong acid electrolyte which can cause corrosion, degradation of catalyst, and other problems that can compromise

efficiency. Problems associated with such conventional liquid direct-feed cells are well recognized in the art.

Jet Propulsion Laboratory (JPL) developed an improved liquid direct-feed cell using a solid-state electrolyte, preferably a solid polymer cation exchange electrolyte membrane. The JPL fuel cell does not use liquid acidic and alkaline electrolyte and hence obviates many problems in the conventional fuel cells. The subject matter of this improvement is described in U.S. Patent No. 5,599,638, U.S. Patent Application Serial No. 08/569,452 (Patent Pending), and U.S. Patent Application Serial No. 08/827,319 (Patent Pending) the disclosures of which are herewith incorporated by reference to the extent necessary for proper understanding.

FIG. 1 illustrates a typical structure of a JPL fuel cell with an anode 110, a solid electrolyte membrane 120, and a cathode 130 enclosed in housing 140. An anode 110 is formed on a first surface 145 of the solid electrolyte membrane 120 with a first catalyst for electro-oxidation. Cathode 130 is formed on a second surface 150 thereof opposing the first surface 145 with a second catalyst for electro-reduction. The anode 110, the solid electrolyte membrane 120, and the cathode 130 are bonded to form a single multi-layer composite structure 160, referred to herein as a membrane electrode assembly (MEA). An electrical load 170 is connected to the anode 110 and cathode 130 for electrical power output.

A fuel pump 180 is provided for pumping an organic fuel and water solution into an anode chamber 190 of housing 140. The organic fuel and water mixture is withdrawn through an outlet port 1100 and is re-circulated. Carbon dioxide formed in the anode chamber

190 is vented through a port 1120 within fuel tank 1130. An oxygen or air compressor 1140 is provided to feed oxygen or air into a cathode chamber 1150 within housing 140.

Prior to use, anode chamber 190 is filled with the organic fuel and water mixture and cathode chamber 1150 is filled with air or oxygen. During operation, the organic fuel is circulated past anode 110 while oxygen or air is pumped into cathode chamber 1150 and circulated past cathode 130. When an electrical load 170 is connected between anode 110 and cathode 130, electro-oxidation of the organic fuel occurs at anode 110 and electro-reduction of oxygen occurs at cathode 130. Electrons generated by electro-oxidation at anode 110 are conducted through the external load 170 and are captured at cathode 130. Hydrogen ions or protons generated at anode 110 are transported directly across the solid electrolyte membrane 120 to cathode 130. Thus, a flow of current is sustained by a flow of ions through the cell and electrons through the external load 170.

As noted above, anode 110, cathode 130 and solid electrolyte membrane 120 form a single composite layered structure 160. In a preferred embodiment, solid electrolyte membrane 120 is formed from NAFION(TM), a perfluorinated proton-exchange membrane material. NAFION(TM) is a co-polymer of tetrafluoroethylene and perfluorovinylether sulfonic acid. Other membrane materials can also be used.

Anode 110 includes a catalyst material applied to an electrode backing substrate. The preferred catalyst used for the anode is platinum-ruthenium. The loading of the catalyst is preferably in the range of 0.5 - 4.0 mg/cm^2. More efficient electro-oxidation is

realized at higher loading levels.

Preferably, commercially available TORAY(TM) paper is used as the electrode backing substrate. This porous carbon backing paper, however, is first pre-processed to improve its water resistant characteristics to reduce fuel crossover. The pre-processing uses a DUPONT(TM) "TEFLON(TM) 30" suspension of about 60% solids. "TEFLON(TM) 30" is added to approximately 17.1 grams of water. The paper is dipped and then sintered in a furnace oven at approximately 350°C for one hour. A processed paper will increase its weight by about 5% over the course of this process. The paper is weighed to determine if sufficient absorption has occurred and/or if further paper processing is needed. This coated substrate forms the eventual electrode.

Cathode 130 is a gas diffusion electrode wherein platinum catalyst is the preferred catalyst material. Like the anode, the catalyst material is applied on an electrode backing substrate. The loading of the catalyst onto the electrode backing substrate is preferably in the range of 0.5-4.0 mg/cm^2. With better performance at 4.0 mg/cm^2. The catalyst material and the electrode backing substrate contain 10-50 weight percent TEFLON(TM) to provide hydrophobicity, creating a three-phase boundary and to achieve efficient removal of water produced by electro-reduction of oxygen.

During operation, a fuel and water mixture containing no acidic or alkaline electrolyte in the concentration range of 0.5 - 3.0 mole/liter is circulated past anode 110 within anode chamber 190. Preferably, flow rates in the range of 10 - 500 ml/min. are used. As the fuel and water mixture circulates past anode 110, the following electrochemical reaction, for an exemplary

methanol cell, occurs releasing electrons:

$$\textit{Anode}:\ CH_3OH + H_20 \Rightarrow C0_2 + 6H^+ + 6e^- \qquad (1)$$

Carbon dioxide produced by the above reaction is withdrawn along with the fuel and water solution through outlet port 1100 and separated from the solution in a gas-liquid separator. The fuel and water solution is then re-circulated into the cell by fuel pump 180.

Simultaneous with the electrochemical reaction described in equation 1 above, another electrochemical reaction involving the electro-reduction of oxygen, which captures electrons, occurs at cathode 130 and is given by:

$$\textit{Cathode}:\ 0_2 + 4H^+ + 4e^- \Rightarrow 2H_20 \qquad (2)$$

The individual electrode reactions described by equations 1 and 2 result in an overall reaction for the exemplary methanol fuel cell given by:

$$\textit{Cell}:\ CH_3OH + 1.50_2 \Rightarrow CO_2 + 2H_2O \qquad (3)$$

In addition to undergoing electro-oxidation at the anode, the liquid fuel which is dissolved in water may pass through catalyst gate structures in the solid electrolyte membrane 120 and may combine with oxygen on the surface of the cathode electrocatalyst. This process is described by equation 3 for the example of methanol. This phenomenon is termed "fuel crossover".

Fuel crossover lowers the operating potential of the oxygen electrode, cathode 130, and results in consumption of fuel without producing useful electrical energy. In general, fuel crossover is a parasitic reaction that lowers efficiency. Fuel crossover reduces performance and generates heat in the fuel cell. Reduction of the rate of fuel crossover is desirable. The rate of fuel crossover is proportional to the permeability of the fuel through the solid electrolyte membrane and increases with increasing fuel concentration and temperature.

Two factors that can affect the commercial value of the direct-feed fuel cell are cost and performance. At the level of the membrane electrode assembly, the former is affected by catalyst loading and the choice of membrane, the latter by voltage and fuel crossover. The present inventors disclose a method and an apparatus that reduce fuel crossover and thereby increase performance efficiency of the fuel cell.

Summary

The inventors disclose processes which aid in reduction of undesirable fuel and water diffusion from the anode to the cathode. These processes reduce fuel crossover by closing catalyst gate structures at the electrode-membrane interface.

One process, multi-layer catalyst application, reduces fuel crossover by applying the catalyst material in multiple layers, forming a multi-layer catalyst formation on the electrode with the densest layer of catalyst near the electrode-membrane interface. The densest catalyst layer serves as a "pore plugger" which closes catalyst gate structures.

Another process, inert pore blocker application, reduces fuel crossover by applying an inert pore blocker layer on top of the catalyst formation at the electrode-membrane interface. This final layer of inert pore plugging material, is preferably made of fine carbon particles.

Both processes fabricate a membrane electrode assembly (MEA) in which the catalyst layers are not uniform. This MEA features non-isotropic distribution of electrode components.

Utilization of the above processes during MEA fabrication can improve fuel cell performance. Fuel crossover can be reduced from 42% to 25%.

Brief Description of the Drawing

The objects and advantages of the present invention will become more readily apparent after reviewing the following detailed description and accompanying drawings, wherein:

FIG. 1 illustrates a direct liquid feed fuel cell;

FIG. 2 shows a membrane electrode assembly (MEA) fabricated by multi-layer catalyst application;

FIG. 3 shows a MEA fabricated by inert pore blocker application.

Description of the Preferred Embodiments

Catalyst gate structures, also referred to as pore structures, allow fuel to enter the MEA to react with the anode catalyst and gas to enter the MEA to react with the cathode catalyst. Pore structures are provided by the electrode backing substrate. The electrode backing substrate is preferably a porous carbon backing paper.

However, pore structures are generally undesirable at the interface between the electrodes and the membrane, referred to herein as the electrode-membrane interface. The pore structures at the interface promote undesirable fuel crossover from the anode to the cathode through the solid electrolyte membrane. Membrane electrode assemblies (MEA) wherein the pore structures on the electrode are closed at the electrode-membrane interface are disclosed.

Major steps in fabricating MEA include: 1) Pre-treating the solid electrolyte membrane with softening and swelling agents; 2) Application of the catalyst material onto the electrode backing substrate; 3) Application of a "pore-plugging" layer; 4) Assembly of MEA by hot press bonding. Each step is described in detail herein.

1. Pre-treating the solid electrolyte membrane with softening & swelling agents.

Solid electrolyte membrane is pre-treated in a solution of 25% isopropanol and water. Solutions ranging from 10-90% isopropanol can also be used. Swelling the membrane before hot press bonding results in shrinkage during hot pressing. This shrinkage provides a "lock and key" bonding between the catalyst and the membrane.

2. Application of the catalyst material onto electrode backing substrate.

The catalyst material is made from mixing a catalyst metal powder with a water-repelling material. In a preferred embodiment, the anode catalyst metal powder is bimetallic having separate platinum particles and separate ruthenium particles which are uniformly mixed. One embodiment uses approximately 60% platinum,

40% ruthenium.

In a preferred embodiment, the catalyst material includes a dilute polytetrafluoroethylene, e.g. TEFLON(TM) 30, suspension of 12 weight percent solids having 1 gram of TEFLON(TM) 30 concentrate to 4 grams of de-ionized water. 300 mg of de-ionized water is added to 350 mg of the 12 weight percent TEFLON(TM) solution. 144 mg of catalyst metal powder is mixed into this solution. The catalyst metal power and TEFLON(TM) mixture is sonicated for 4 minutes. The catalyst material is then applied onto one side of a 2-inch by 2-inch piece of plain TGPH-90 or 060 paper which is manufactured by Toray Inc. The catalyst material applied onto the electrode backing substrate forms the electrode.

The cathode uses a preferred catalyst material including platinum catalyst and TEFLON(TM) prepared similarly to the catalyst material for the anode. The catalyst material is applied to a 5 weight percent teflonized electrode backing substrate, preferably a porous carbon backing paper. Teflonized electrode backing substrate reduces fuel crossover.

After application of the catalyst material onto the electrode backing, the resulting electrode is sintered at around 350 degrees Celsius. TEFLON(TM) binds the catalyst material onto the electrode. Sintering burns off surfactants. Sintering also improves TEFLON(TM)'s hydrophobicity. Exposure to high temperatures improves TEFLON(TM)'s bonding ability thereby preventing catalyst migration during hot press bonding.

After the catalyst material dries and the electrode cools to room temperature, an ionomer solution is applied onto the electrode. Preferably, a solution of

perflurosulfonic acid, NAFION(TM), is used. NAFION(TM) improves ion conduction resulting in better performance. Since NAFION(TM) can not tolerate the sintering process, NAFION(TM) is applied afterwards.

<u>3. Application of a "pore-plugging" layer.</u>

The inventors want the fuel at the anode side to reach the catalyst. At the same time, it is not allowed past the electrode-membrane interface. Processes that address these concerns are described herein.

Multi-layer Catalyst Application

The pore structures at the electrode-membrane interface are modified by application of an asymmetric layer of catalyst at the interface. The asymmetric layer is formed by a plurality of varying density. For example, starting with the initial catalyst layer application onto the electrode backing substrate, each successive layers of catalyst applied is denser than the layer before. The last catalyst layer applied is the densest. Each application follows the steps disclosed above where the electrode is sintered after the catalyst material is applied, then cooled before the ionomer is applied onto the electrode backing substrate. The resulting product is an electrode with an asymmetric, non-isotropic distribution of electrode components, namely, varying densities of catalyst layers.

Both the anode and the cathode are fabricated to have this multi-layer catalyst formation as shown in FIG. 2. When fully assembled using the multi-layer catalyst application, the membrane electrode assembly 160 has a solid electrolyte membrane 120 with two surfaces. The first membrane surface 145 is in contact with the densest catalyst layer 220 of a multi-layer catalyst formation

210 of the anode 110. The densest catalyst layer 220 is at the electrode-membrane interface 230 between the anode 110 and the membrane 120. The anode 110 comprises a multi-layer catalyst formation 210 coated on an electrode backing substrate 240.

The second membrane surface 150, positioned on the opposite side of the first membrane surface 145, is in contact with the densest catalyst layer 260 of a multi-layer catalyst formation 250 of the cathode 130. Similarly, the densest catalyst layer 260 is at the electrode-membrane interface 270 between the cathode 130 and the membrane 120. The cathode 130 comprises the multi-layer catalyst formation 250 coated on the electrode backing substrate 280.

Inert Pore Blocker Application

An MEA fabricated by inert pore blocker application is shown in FIG. 3. Catalyst materials are applied onto the electrode backing substrate 240 of the anode 110 and the electrode backing substrate 280 of the cathode 130. The resulting catalyst formation 310 of the anode 110 and catalyst formation 330 of the cathode 130 are allowed to dry.

Pore structures are then blocked by applying a final layer of inert material preferably made of very fine particles on top of the catalyst formation at the electrode-membrane interface. These particles make up the inert pore blocker layer; the particles will penetrate and plug the pore structures at the electrode-membrane interface. Inert materials used in the preferred embodiment are very fine carbon particles. The resulting product is an electrode with an asymmetric, non-isotropic distribution of electrode components,

namely, a catalyst formation and an inert pore blocker layer.

Both the anode and the cathode are fabricated to incorporate these components as shown in FIG. 3. When fully assembled using the inert pore blocker application, the membrane electrode assembly 160 has a solid electrolyte membrane 120 with two surfaces. The first membrane surface 145 is in contact with the catalyst formation 310 face of the anode 110. The inert pore blocker layer 320 is at the anode-membrane interface 230. The anode 110 comprises the inert pore blocker layer 320, the catalyst formation 310, and the electrode backing substrate 240.

The second membrane surface 150, positioned on the opposite side of the first membrane surface 145, is in contact with the catalyst formation 330 face of the cathode 130. The inert pore blocker layer 340 is at the cathode-membrane interface 270. The cathode 130 comprises the inert pore blocker layer 340, the catalyst formation 330, and the electrode backing substrate 280.

4. Assembly of MEA by hot press bonding.

The pre-treated membrane is sandwiched between the catalyst coated anode and cathode supports and held in a press for 10 minutes under a pressure that can vary from 500 psi- 1500 psi. For papers that are thin, such as the TGPH-060 (six millimeters thick), the preferred pressures are close to 500 psi. With thicker papers the optimum pressures are as high as 1250 psi.

After 10 minutes of pressure, heating is commenced. The heat is slowly ramped up to about 145°C. The slow ramping up should take place over 25-30 minutes, with the last 5 minutes of heating being a time of

temperature stabilization. The heat is switched off, but the pressure is maintained. The press is then rapidly cooled using circulating water while the pressure is maintained. On cooling to about 60°C, the membrane electrode assembly is removed from the press and stored in water in a sealed plastic bag.

Although only a few embodiments have been described in detail above, those having ordinary skill in the art will certainly understand that many modifications are possible in the preferred embodiment without departing from the teachings thereof.

All such modifications are intended to be encompassed within the following claims.

What is claimed is:

1. A membrane electrode assembly for direct feed fuel cells, comprising:

a solid electrolyte membrane having a first membrane surface and a second membrane surface;

a first electrode backing substrate positioned at said first membrane surface forming a first electrode-membrane interface;

a second electrode backing substrate positioned at said second membrane surface forming a second electrode-membrane interface;

an anode formed on said first membrane surface, said anode having a first multi-layer catalyst formation with non-uniform densities applied on said first electrode backing substrate at said first electrode-membrane interface;

a cathode formed on said second membrane surface, said cathode having a second multi-layer catalyst formation with non-uniform densities applied on said second electrode backing substrate at said second electrode-membrane interface.

2. An apparatus as in claim 1, wherein said first electrode backing substrate is plain TGPH-090 or 060 porous carbon paper.

3. An apparatus as in claim 1, wherein said second electrode backing substrate is teflonized TGPH-090 or 060 porous carbon paper.

4. An apparatus as in claim 1, wherein said first and second multi-layer catalyst formation include:

a first catalyst layer formed on said first and second electrode backing substrate;

subsequent denser catalyst layers formed on top of said first catalyst layer on said first and second electrode backing substrate;

a last densest catalyst layer formed on top of said subsequent denser catalyst layers at said first and second electrode-membrane interface.

5. A method of forming an electrode for a fuel cell, comprising:

first obtaining a catalyst mixture, wherein said catalyst mixture includes a catalyst metal powder and a water-repelling material;

second obtaining an electrode backing substrate;

first applying said catalyst mixture onto said electrode backing substrate;

sintering said catalyst mixture on said electrode backing substrate;

second applying an ionomer after said sintering forming a first catalyst layer;

first depositing subsequent denser catalyst layers on top of said first catalyst layer;

second depositing a last densest catalyst layer on top of said subsequent catalyst layers.

6. A method as in claim 5, wherein said water-repelling material is polytetrafluoroethylene (PTFE).

7. A method as in claim 5, wherein said ionomer is a perflurosulfonic acid solution.

8. A method as in claim 5, wherein said sintering occurs at approximately 350 degrees Celsius and under nitrogen gas.

9. A method of fabricating a membrane electrode assembly, comprising:

first obtaining a solid electrolyte membrane having a first and second membrane surface;

second obtaining a first and second electrode backing substrate;

third obtaining a first and second catalyst ink;

first applying said first catalyst ink on said first electrode backing substrate forming a first initial catalyst layer;

first forming first subsequent denser catalyst layers on top of said first initial catalyst layer on said first electrode backing substrate;

second forming a first final densest catalyst layer on top of said first subsequent denser catalyst layers;

second applying said second catalyst ink on said second electrode backing substrate forming a second initial catalyst layer;

third forming second subsequent denser catalyst layers on top of said second initial catalyst layer on said second electrode backing substrate;

fourth forming a second final densest catalyst layer on top of said second subsequent denser catalyst layers;

placing said membrane between said first and second electrode backing substrate;

bonding said membrane, said first and second electrode backing substrate to form a membrane electrode

assembly.

10. A membrane electrode assembly for direct feed fuel cells, comprising:

a solid electrolyte membrane having a first membrane surface and a second membrane surface;

a first electrode backing substrate positioned at said first membrane surface forming a first electrode-membrane interface, wherein said first electrode backing substrate has first pore structures;

a second electrode backing substrate positioned at said second membrane surface forming a second electrode-membrane interface, wherein said second electrode backing substrate has second pore structures;

an anode formed on said first membrane surface, said anode having a first catalyst formation and a first inert pore blocker layer applied on said first electrode backing substrate at said first electrode-membrane interface;

a cathode formed on said second membrane surface, said cathode having a second catalyst formation and a second inert pore blocker layer applied on said second electrode backing substrate at said second electrode-membrane interface.

11. An apparatus as in claim 10, wherein said first electrode backing substrate is plain TGPH-090 or 060 porous carbon paper.

12. An apparatus as in claim 10, wherein said second electrode backing substrate is teflonized TGPH-090 or 060 porous carbon paper.

13. An apparatus as in claim 10, wherein said first inert pore blocker is made of fine particles positioned to block said first pore structures on said first electrode backing substrate at said first electrode-membrane interface.

14. An apparatus as in claim 10, wherein said second inert pore blocker is made of fine particles positioned to block said second pore structures on said second electrode backing substrate at said second electrode-membrane interface.

15. A method of forming an electrode for a fuel cell, comprising:

first obtaining a catalyst mixture;

second obtaining a inert pore blocker material, wherein said material include fine particles;

third obtaining an electrode backing substrate;

first applying said catalyst mixture onto said electrode backing substrate forming a catalyst formation;

second applying said inert pore blocker material on top of said catalyst formation.

16. A method as in claim 15, further comprising:

sintering said electrode backing substrate after said first applying and before said second applying;

third applying an ionomer layer onto said electrode backing substrate after said sintering and before said second applying.

17. A method as in claim 16, wherein said sintering occurs at approximately 350 degrees Celsius and under nitrogen gas.

18. A method as in claim 9, wherein said solid electrolyte membrane is pre-treated with a softening and swelling agent.

19. A method as in claim 18, wherein said softening and swelling agent is an isopropanol solution with a concentration ranging from 10-90% isopropanol.

20. A method of fabricating a membrane electrode assembly, comprising:

first obtaining a solid electrolyte membrane having a first and a second membrane surface;

second obtaining a first and second electrode backing substrate;

third obtaining a first and second catalyst ink;

fourth obtaining an inert pore blocker material;

first applying said first catalyst ink on said first electrode backing substrate forming a first catalyst formation;

second applying said inert pore blocker material on top of said first catalyst formation;

third applying said second catalyst ink on said second electrode backing substrate forming a second catalyst formation;

fourth applying said inert pore blocker material on top of said second catalyst formation;

placing said membrane between said first and second electrode backing substrate;

bonding said membrane, said first and second electrode backing substrate to form a membrane electrode assembly.

21. A method as in claim 20, wherein said solid electrolyte membrane is pre-treated with a softening and swelling agent.

22. A method as in claim 21, wherein said softening and swelling agent is an isopropanol solution with a concentration ranging from 10-90% isopropanol.

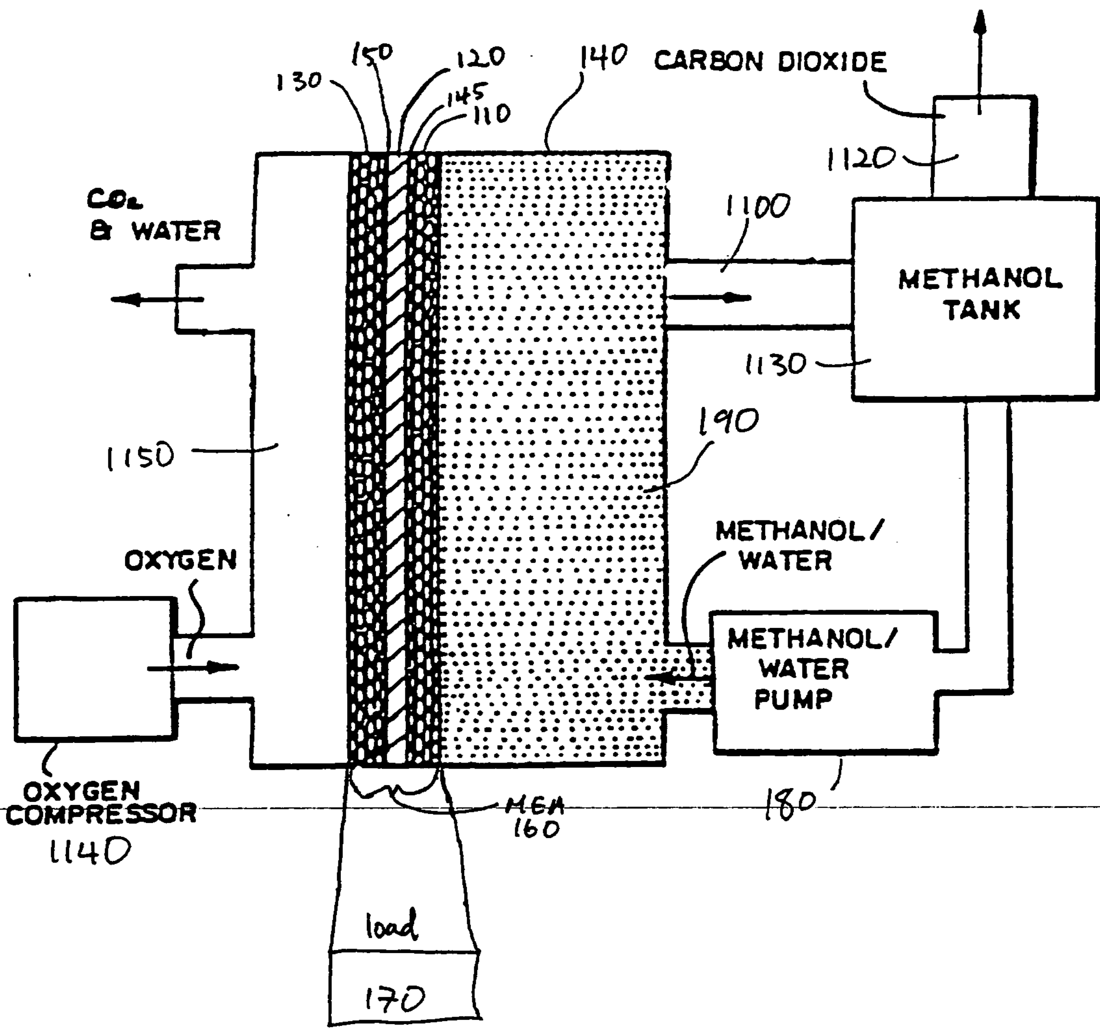
130
150
120
145
110
140
CARBON DIOXIDE
1120
CO_2 & WATER
1100
METHANOL TANK
1130
1150
190
METHANOL/ WATER
OXYGEN
METHANOL/ WATER PUMP
OXYGEN COMPRESSOR
1140
MEA 160
180
load
170

FIG. 1

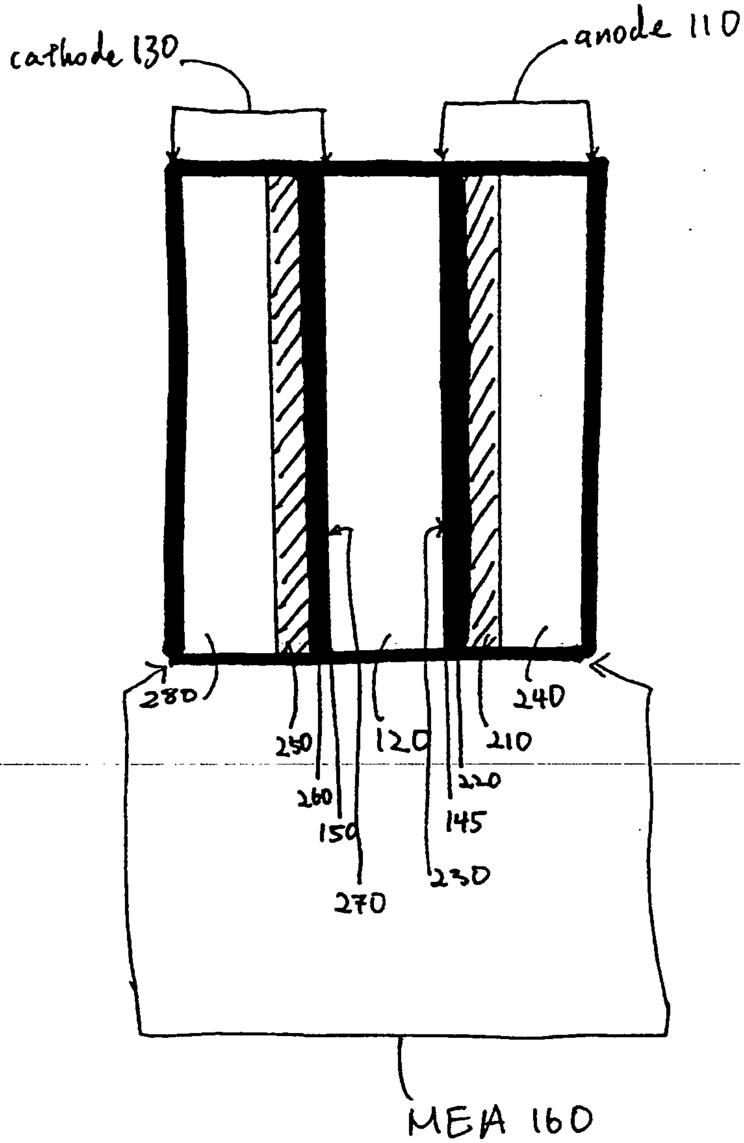

FIG. 2
Multi-layer Catalyst Application

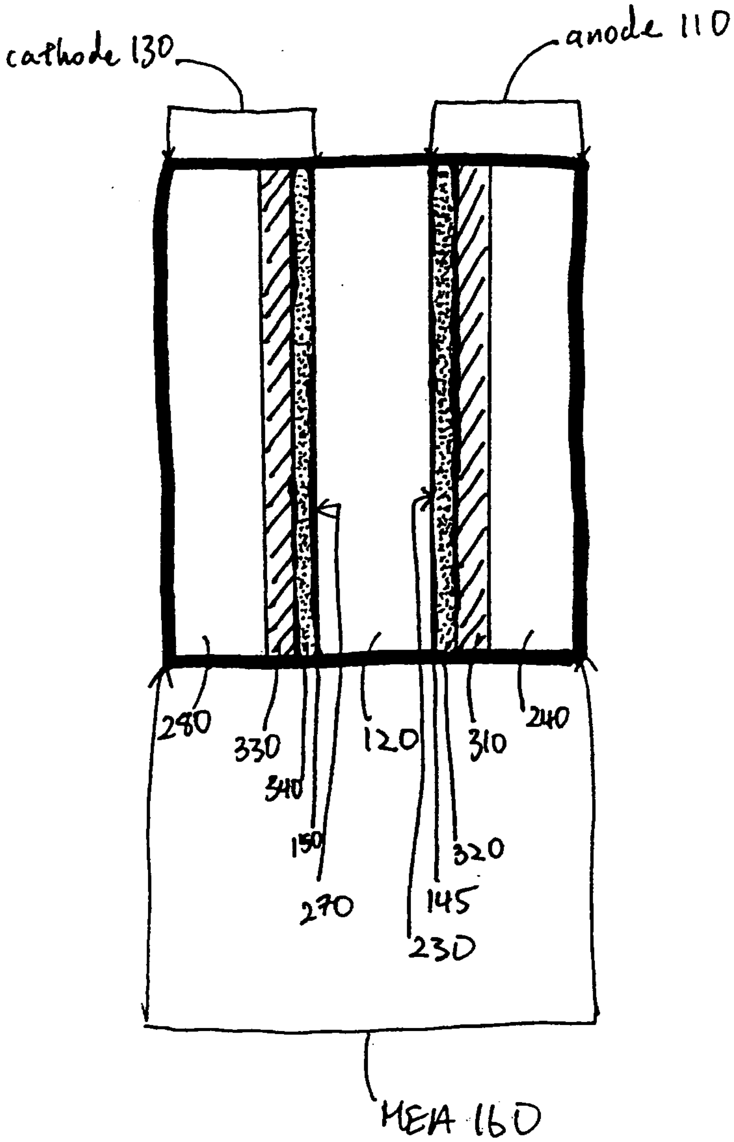

FIG. 3
Inert Pore Blocker Application

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/02677

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C25B 11/03, 11/00, 11/12, 13/00; H01M 8/10, 4/86; B05D 5/12
US CL :204/283, 284, 290R, 294, 296; 429/33, 40, 41, 42, 44; 427/115
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/283, 284, 290R, 294, 296; 429/33, 40, 41, 42, 44; 427/115

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,599,638 A (SURAMPUDI et al) 04 February 1997.	1-22
A	US 5,336,384 A (TSOU et al) 09 August 1994.	1-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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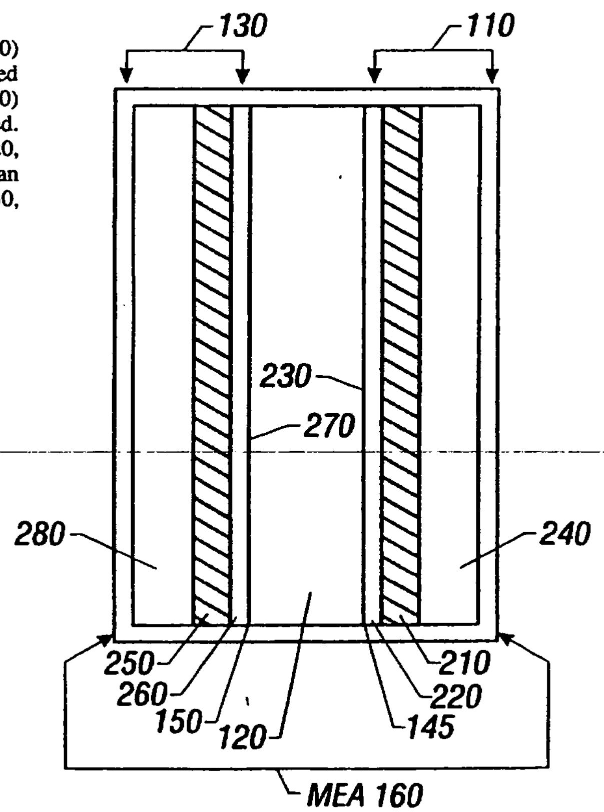
(57) Abstract

An improved direct–feed fuel cell having a solid membrane electrolyte (120) for electrochemical reactions of an organic fuel. Fuel crossover has been reduced due to pore structures blockage at the electrode–membrane interfaces (230, 270) of the membrane electrode assembly (160). Two improved MEA's are disclosed. One utilizes a multi–layer catalyst formation with a densest catalyst layer (220, 260) applied at the electrode–catalyst interfaces (230, 270). Another utilizes an inert pore blocking layer (320, 340) at the electrode–membrane interfaces (230, 270).



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Asymmetric Electrodes for Direct-Feed Fuel Cells

Origin of Invention

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

Field

This disclosure generally relates to organic fuel cells for use in the generation of electrical energy and in particular liquid direct-feed organic fuel cells and the manufacturing thereof.

Background

Fuel cells are electrochemical cells in which a free energy change resulting from a fuel oxidation reaction is converted into electrical energy. Fuel cells use renewable fuels such as methanol; typical products from the electrochemical reactions include carbon dioxide and water. Fuel cells may be an attractive alternative to the combustion of fossil fuels.

Previously, fuel cells used reformers to convert methanol into hydrogen gas for use by fuel cells. Direct oxidation fuel cells can offer weight and volume advantage over the indirect reformer fuel cells. However, initial direct oxidation models used a strong acid electrolyte which can cause corrosion, degradation of catalyst, and other problems that can compromise

efficiency. Problems associated with such conventional liquid direct-feed cells are well recognized in the art.

Jet Propulsion Laboratory (JPL) developed an improved liquid direct-feed cell using a solid-state electrolyte, preferably a solid polymer cation exchange electrolyte membrane. The JPL fuel cell does not use liquid acidic and alkaline electrolyte and hence obviates many problems in the conventional fuel cells. The subject matter of this improvement is described in U.S. Patent No. 5,599,638, U.S. Patent Application Serial No. 08/569,452 (Patent Pending), and U.S. Patent Application Serial No. 08/827,319 (Patent Pending) the disclosures of which are herewith incorporated by reference to the extent necessary for proper understanding.

FIG. 1 illustrates a typical structure of a JPL fuel cell with an anode 110, a solid electrolyte membrane 120, and a cathode 130 enclosed in housing 140. An anode 110 is formed on a first surface 145 of the solid electrolyte membrane 120 with a first catalyst for electro-oxidation. Cathode 130 is formed on a second surface 150 thereof opposing the first surface 145 with a second catalyst for electro-reduction. The anode 110, the solid electrolyte membrane 120, and the cathode 130 are bonded to form a single multi-layer composite structure 160, referred to herein as a membrane electrode assembly (MEA). An electrical load 170 is connected to the anode 110 and cathode 130 for electrical power output.

A fuel pump 180 is provided for pumping an organic fuel and water solution into an anode chamber 190 of housing 140. The organic fuel and water mixture is withdrawn through an outlet port 1100 and is re-circulated. Carbon dioxide formed in the anode chamber

190 is vented through a port 1120 within fuel tank 1130. An oxygen or air compressor 1140 is provided to feed oxygen or air into a cathode chamber 1150 within housing 140.

Prior to use, anode chamber 190 is filled with the organic fuel and water mixture and cathode chamber 1150 is filled with air or oxygen. During operation, the organic fuel is circulated past anode 110 while oxygen or air is pumped into cathode chamber 1150 and circulated past cathode 130. When an electrical load 170 is connected between anode 110 and cathode 130, electro-oxidation of the organic fuel occurs at anode 110 and electro-reduction of oxygen occurs at cathode 130. Electrons generated by electro-oxidation at anode 110 are conducted through the external load 170 and are captured at cathode 130. Hydrogen ions or protons generated at anode 110 are transported directly across the solid electrolyte membrane 120 to cathode 130. Thus, a flow of current is sustained by a flow of ions through the cell and electrons through the external load 170.

As noted above, anode 110, cathode 130 and solid electrolyte membrane 120 form a single composite layered structure 160. In a preferred embodiment, solid electrolyte membrane 120 is formed from NAFION(TM), a perfluorinated proton-exchange membrane material. NAFION(TM) is a co-polymer of tetrafluoroethylene and perfluorovinylether sulfonic acid. Other membrane ~~materials can also be used.~~

Anode 110 includes a catalyst material applied to an electrode backing substrate. The preferred catalyst used for the anode is platinum-ruthenium. The loading of the catalyst is preferably in the range of 0.5 - 4.0 mg/cm^2. More efficient electro-oxidation is

realized at higher loading levels.

Preferably, commercially available TORAY(TM) paper is used as the electrode backing substrate. This porous carbon backing paper, however, is first pre-processed to improve its water resistant characteristics to reduce fuel crossover. The pre-processing uses a DUPONT(TM) "TEFLON(TM) 30" suspension of about 60% solids. "TEFLON(TM) 30" is added to approximately 17.1 grams of water. The paper is dipped and then sintered in a furnace oven at approximately 350°C for one hour. A processed paper will increase its weight by about 5% over the course of this process. The paper is weighed to determine if sufficient absorption has occurred and/or if further paper processing is needed. This coated substrate forms the eventual electrode.

Cathode 130 is a gas diffusion electrode wherein platinum catalyst is the preferred catalyst material. Like the anode, the catalyst material is applied on an electrode backing substrate. The loading of the catalyst onto the electrode backing substrate is preferably in the range of 0.5-4.0 mg/cm^2. With better performance at 4.0 mg/cm^2. The catalyst material and the electrode backing substrate contain 10-50 weight percent TEFLON(TM) to provide hydrophobicity, creating a three-phase boundary and to achieve efficient removal of water produced by electro-reduction of oxygen.

During operation, a fuel and water mixture containing no acidic or alkaline electrolyte in the concentration range of 0.5 - 3.0 mole/liter is circulated past anode 110 within anode chamber 190. Preferably, flow rates in the range of 10 - 500 ml/min. are used. As the fuel and water mixture circulates past anode 110, the following electrochemical reaction, for an exemplary

methanol cell, occurs releasing electrons:

$$Anode{:}\quad CH_3OH + H_20 \Rightarrow C0_2 + 6H^+ + 6e^- \qquad (1)$$

Carbon dioxide produced by the above reaction is withdrawn along with the fuel and water solution through outlet port 1100 and separated from the solution in a gas-liquid separator. The fuel and water solution is then re-circulated into the cell by fuel pump 180.

Simultaneous with the electrochemical reaction described in equation 1 above, another electrochemical reaction involving the electro-reduction of oxygen, which captures electrons, occurs at cathode 130 and is given by:

$$Cathode{:}\quad 0_2 + 4H^+ + 4e^- \Rightarrow 2H_20 \qquad (2)$$

The individual electrode reactions described by equations 1 and 2 result in an overall reaction for the exemplary methanol fuel cell given by:

$$Cell{:}\quad CH_3OH + 1.50_2 \Rightarrow CO_2 + 2H_2O \qquad (3)$$

In addition to undergoing electro-oxidation at the anode, the liquid fuel which is dissolved in water may pass through catalyst gate structures in the solid electrolyte membrane 120 and may combine with oxygen on the surface of the cathode electrocatalyst. This process is described by equation 3 for the example of methanol. This phenomenon is termed "fuel crossover".

Fuel crossover lowers the operating potential of the oxygen electrode, cathode 130, and results in consumption of fuel without producing useful electrical energy. In general, fuel crossover is a parasitic reaction that lowers efficiency. Fuel crossover reduces performance and generates heat in the fuel cell. Reduction of the rate of fuel crossover is desirable. The rate of fuel crossover is proportional to the permeability of the fuel through the solid electrolyte membrane and increases with increasing fuel concentration and temperature.

Two factors that can affect the commercial value of the direct-feed fuel cell are cost and performance. At the level of the membrane electrode assembly, the former is affected by catalyst loading and the choice of membrane, the latter by voltage and fuel crossover. The present inventors disclose a method and an apparatus that reduce fuel crossover and thereby increase performance efficiency of the fuel cell.

Summary

The inventors disclose processes which aid in reduction of undesirable fuel and water diffusion from the anode to the cathode. These processes reduce fuel crossover by closing catalyst gate structures at the electrode-membrane interface.

One process, multi-layer catalyst application, reduces fuel crossover by applying the catalyst material in multiple layers, forming a multi-layer catalyst formation on the electrode with the densest layer of catalyst near the electrode-membrane interface. The densest catalyst layer serves as a "pore plugger" which closes catalyst gate structures.

Another process, inert pore blocker application, reduces fuel crossover by applying an inert pore blocker layer on top of the catalyst formation at the electrode-membrane interface. This final layer of inert pore plugging material, is preferably made of fine carbon particles.

Both processes fabricate a membrane electrode assembly (MEA) in which the catalyst layers are not uniform. This MEA features non-isotropic distribution of electrode components.

Utilization of the above processes during MEA fabrication can improve fuel cell performance. Fuel crossover can be reduced from 42% to 25%.

Brief Description of the Drawing

The objects and advantages of the present invention will become more readily apparent after reviewing the following detailed description and accompanying drawings, wherein:

FIG. 1 illustrates a direct liquid feed fuel cell;

FIG. 2 shows a membrane electrode assembly (MEA) fabricated by multi-layer catalyst application;

FIG. 3 shows a MEA fabricated by inert pore blocker application.

Description of the Preferred Embodiments

Catalyst gate structures, also referred to as pore structures, allow fuel to enter the MEA to react with the anode catalyst and gas to enter the MEA to react with the cathode catalyst. Pore structures are provided by the electrode backing substrate. The electrode backing substrate is preferably a porous carbon backing paper.

However, pore structures are generally undesirable at the interface between the electrodes and the membrane, referred to herein as the electrode-membrane interface. The pore structures at the interface promote undesirable fuel crossover from the anode to the cathode through the solid electrolyte membrane. Membrane electrode assemblies (MEA) wherein the pore structures on the electrode are closed at the electrode-membrane interface are disclosed.

Major steps in fabricating MEA include: 1) Pre-treating the solid electrolyte membrane with softening and swelling agents; 2) Application of the catalyst material onto the electrode backing substrate; 3) Application of a "pore-plugging" layer; 4) Assembly of MEA by hot press bonding. Each step is described in detail herein.

<u>1. Pre-treating the solid electrolyte membrane with softening & swelling agents.</u>

Solid electrolyte membrane is pre-treated in a solution of 25% isopropanol and water. Solutions ranging from 10-90% isopropanol can also be used. Swelling the membrane before hot press bonding results in shrinkage during hot pressing. This shrinkage provides a "lock and key" bonding between the catalyst and the membrane.

<u>2. Application of the catalyst material onto electrode backing substrate.</u>

The catalyst material is made from mixing a catalyst metal powder with a water-repelling material. In a preferred embodiment, the anode catalyst metal powder is bimetallic having separate platinum particles and separate ruthenium particles which are uniformly mixed. One embodiment uses approximately 60% platinum,

40% ruthenium.

In a preferred embodiment, the catalyst material includes a dilute polytetrafluoroethylene, e.g. TEFLON(TM) 30, suspension of 12 weight percent solids having 1 gram of TEFLON(TM) 30 concentrate to 4 grams of de-ionized water. 300 mg of de-ionized water is added to 350 mg of the 12 weight percent TEFLON(TM) solution. 144 mg of catalyst metal powder is mixed into this solution. The catalyst metal power and TEFLON(TM) mixture is sonicated for 4 minutes. The catalyst material is then applied onto one side of a 2-inch by 2-inch piece of plain TGPH-90 or 060 paper which is manufactured by Toray Inc. The catalyst material applied onto the electrode backing substrate forms the electrode.

The cathode uses a preferred catalyst material including platinum catalyst and TEFLON(TM) prepared similarly to the catalyst material for the anode. The catalyst material is applied to a 5 weight percent teflonized electrode backing substrate, preferably a porous carbon backing paper. Teflonized electrode backing substrate reduces fuel crossover.

After application of the catalyst material onto the electrode backing, the resulting electrode is sintered at around 350 degrees Celsius. TEFLON(TM) binds the catalyst material onto the electrode. Sintering burns off surfactants. Sintering also improves TEFLON(TM)'s hydrophobicity. Exposure to high temperatures improves TEFLON(TM)'s bonding ability thereby preventing catalyst migration during hot press bonding.

After the catalyst material dries and the electrode cools to room temperature, an ionomer solution is applied onto the electrode. Preferably, a solution of

perflurosulfonic acid, NAFION(TM), is used. NAFION(TM) improves ion conduction resulting in better performance. Since NAFION(TM) can not tolerate the sintering process, NAFION(TM) is applied afterwards.

3. Application of a "pore-plugging" layer.

The inventors want the fuel at the anode side to reach the catalyst. At the same time, it is not allowed past the electrode-membrane interface. Processes that address these concerns are described herein.

Multi-layer Catalyst Application

The pore structures at the electrode-membrane interface are modified by application of an asymmetric layer of catalyst at the interface. The asymmetric layer is formed by a plurality of varying density. For example, starting with the initial catalyst layer application onto the electrode backing substrate, each successive layers of catalyst applied is denser than the layer before. The last catalyst layer applied is the densest. Each application follows the steps disclosed above where the electrode is sintered after the catalyst material is applied, then cooled before the ionomer is applied onto the electrode backing substrate. The resulting product is an electrode with an asymmetric, non-isotropic distribution of electrode components, namely, varying densities of catalyst layers.

Both the anode and the cathode are fabricated to have this multi-layer catalyst formation as shown in FIG. 2. When fully assembled using the multi-layer catalyst application, the membrane electrode assembly 160 has a solid electrolyte membrane 120 with two surfaces. The first membrane surface 145 is in contact with the densest catalyst layer 220 of a multi-layer catalyst formation

210 of the anode 110. The densest catalyst layer 220 is at the electrode-membrane interface 230 between the anode 110 and the membrane 120. The anode 110 comprises a multi-layer catalyst formation 210 coated on an electrode backing substrate 240.

The second membrane surface 150, positioned on the opposite side of the first membrane surface 145, is in contact with the densest catalyst layer 260 of a multi-layer catalyst formation 250 of the cathode 130. Similarly, the densest catalyst layer 260 is at the electrode-membrane interface 270 between the cathode 130 and the membrane 120. The cathode 130 comprises the multi-layer catalyst formation 250 coated on the electrode backing substrate 280.

Inert Pore Blocker Application

An MEA fabricated by inert pore blocker application is shown in FIG. 3. Catalyst materials are applied onto the electrode backing substrate 240 of the anode 110 and the electrode backing substrate 280 of the cathode 130. The resulting catalyst formation 310 of the anode 110 and catalyst formation 330 of the cathode 130 are allowed to dry.

Pore structures are then blocked by applying a final layer of inert material preferably made of very fine particles on top of the catalyst formation at the electrode-membrane interface. These particles make up the inert pore blocker layer; the particles will penetrate and plug the pore structures at the electrode-membrane interface. Inert materials used in the preferred embodiment are very fine carbon particles. The resulting product is an electrode with an asymmetric, non-isotropic distribution of electrode components,

namely, a catalyst formation and an inert pore blocker layer.

Both the anode and the cathode are fabricated to incorporate these components as shown in FIG. 3. When fully assembled using the inert pore blocker application, the membrane electrode assembly 160 has a solid electrolyte membrane 120 with two surfaces. The first membrane surface 145 is in contact with the catalyst formation 310 face of the anode 110. The inert pore blocker layer 320 is at the anode-membrane interface 230. The anode 110 comprises the inert pore blocker layer 320, the catalyst formation 310, and the electrode backing substrate 240.

The second membrane surface 150, positioned on the opposite side of the first membrane surface 145, is in contact with the catalyst formation 330 face of the cathode 130. The inert pore blocker layer 340 is at the cathode-membrane interface 270. The cathode 130 comprises the inert pore blocker layer 340, the catalyst formation 330, and the electrode backing substrate 280.

4. Assembly of MEA by hot press bonding.

The pre-treated membrane is sandwiched between the catalyst coated anode and cathode supports and held in a press for 10 minutes under a pressure that can vary from 500 psi- 1500 psi. For papers that are thin, such as the TGPH-060 (six millimeters thick), the preferred pressures are close to 500 psi. With thicker papers the optimum pressures are as high as 1250 psi.

After 10 minutes of pressure, heating is commenced. The heat is slowly ramped up to about 145°C. The slow ramping up should take place over 25-30 minutes, with the last 5 minutes of heating being a time of

temperature stabilization. The heat is switched off, but the pressure is maintained. The press is then rapidly cooled using circulating water while the pressure is maintained. On cooling to about 60°C, the membrane electrode assembly is removed from the press and stored in water in a sealed plastic bag.

Although only a few embodiments have been described in detail above, those having ordinary skill in the art will certainly understand that many modifications are possible in the preferred embodiment without departing from the teachings thereof.

All such modifications are intended to be encompassed within the following claims.

<u>What is claimed is:</u>

1. A membrane electrode assembly for direct feed fuel cells, comprising:

a solid electrolyte membrane having a first membrane surface and a second membrane surface;

a first electrode backing substrate positioned at said first membrane surface forming a first electrode-membrane interface;

a second electrode backing substrate positioned at said second membrane surface forming a second electrode-membrane interface;

an anode formed on said first membrane surface, said anode having a first multi-layer catalyst formation with non-uniform densities applied on said first electrode backing substrate at said first electrode-membrane interface;

a cathode formed on said second membrane surface, said cathode having a second multi-layer catalyst formation with non-uniform densities applied on said second electrode backing substrate at said second electrode-membrane interface.

2. An apparatus as in claim 1, wherein said first electrode backing substrate is plain TGPH-090 or 060 porous carbon paper.

3. An apparatus as in claim 1, wherein said second electrode backing substrate is teflonized TGPH-090 or 060 porous carbon paper.

4. An apparatus as in claim 1, wherein said first and second multi-layer catalyst formation include:

a first catalyst layer formed on said first and second electrode backing substrate;

subsequent denser catalyst layers formed on top of said first catalyst layer on said first and second electrode backing substrate;

a last densest catalyst layer formed on top of said subsequent denser catalyst layers at said first and second electrode-membrane interface.

5. A method of forming an electrode for a fuel cell, comprising:

first obtaining a catalyst mixture, wherein said catalyst mixture includes a catalyst metal powder and a water-repelling material;

second obtaining an electrode backing substrate;

first applying said catalyst mixture onto said electrode backing substrate;

sintering said catalyst mixture on said electrode backing substrate;

second applying an ionomer after said sintering forming a first catalyst layer;

first depositing subsequent denser catalyst layers on top of said first catalyst layer;

second depositing a last densest catalyst layer on top of said subsequent catalyst layers.

6. A method as in claim 5, wherein said water-repelling material is polytetrafluoroethylene (PTFE).

7. A method as in claim 5, wherein said ionomer is a perflurosulfonic acid solution.

8. A method as in claim 5, wherein said sintering occurs at approximately 350 degrees Celsius and under nitrogen gas.

9. A method of fabricating a membrane electrode assembly, comprising:

first obtaining a solid electrolyte membrane having a first and second membrane surface;

second obtaining a first and second electrode backing substrate;

third obtaining a first and second catalyst ink;

first applying said first catalyst ink on said first electrode backing substrate forming a first initial catalyst layer;

first forming first subsequent denser catalyst layers on top of said first initial catalyst layer on said first electrode backing substrate;

second forming a first final densest catalyst layer on top of said first subsequent denser catalyst layers;

second applying said second catalyst ink on said second electrode backing substrate forming a second initial catalyst layer;

third forming second subsequent denser catalyst layers on top of said second initial catalyst layer on said second electrode backing substrate;

fourth forming a second final densest catalyst layer on top of said second subsequent denser catalyst layers;

placing said membrane between said first and second electrode backing substrate;

bonding said membrane, said first and second electrode backing substrate to form a membrane electrode

assembly.

10. A membrane electrode assembly for direct feed fuel cells, comprising:

a solid electrolyte membrane having a first membrane surface and a second membrane surface;

a first electrode backing substrate positioned at said first membrane surface forming a first electrode-membrane interface, wherein said first electrode backing substrate has first pore structures;

a second electrode backing substrate positioned at said second membrane surface forming a second electrode-membrane interface, wherein said second electrode backing substrate has second pore structures;

an anode formed on said first membrane surface, said anode having a first catalyst formation and a first inert pore blocker layer applied on said first electrode backing substrate at said first electrode-membrane interface;

a cathode formed on said second membrane surface, said cathode having a second catalyst formation and a second inert pore blocker layer applied on said second electrode backing substrate at said second electrode-membrane interface.

11. An apparatus as in claim 10, wherein said first electrode backing substrate is plain TGPH-090 or 060 porous carbon paper.

12. An apparatus as in claim 10, wherein said second electrode backing substrate is teflonized TGPH-090 or 060 porous carbon paper.

13. An apparatus as in claim 10, wherein said first inert pore blocker is made of fine particles positioned to block said first pore structures on said first electrode backing substrate at said first electrode-membrane interface.

14. An apparatus as in claim 10, wherein said second inert pore blocker is made of fine particles positioned to block said second pore structures on said second electrode backing substrate at said second electrode-membrane interface.

15. A method of forming an electrode for a fuel cell, comprising:

first obtaining a catalyst mixture;

second obtaining a inert pore blocker material, wherein said material include fine particles;

third obtaining an electrode backing substrate;

first applying said catalyst mixture onto said electrode backing substrate forming a catalyst formation;

second applying said inert pore blocker material on top of said catalyst formation.

16. A method as in claim 15, further comprising:

sintering said electrode backing substrate after said first applying and before said second applying;

third applying an ionomer layer onto said electrode backing substrate after said sintering and before said second applying.

17. A method as in claim 16, wherein said sintering occurs at approximately 350 degrees Celsius and under nitrogen gas.

18. A method as in claim 9, wherein said solid electrolyte membrane is pre-treated with a softening and swelling agent.

19. A method as in claim 18, wherein said softening and swelling agent is an isopropanol solution with a concentration ranging from 10-90% isopropanol.

20. A method of fabricating a membrane electrode assembly, comprising:

first obtaining a solid electrolyte membrane having a first and a second membrane surface;

second obtaining a first and second electrode backing substrate;

third obtaining a first and second catalyst ink;

fourth obtaining an inert pore blocker material;

first applying said first catalyst ink on said first electrode backing substrate forming a first catalyst formation;

second applying said inert pore blocker material on top of said first catalyst formation;

third applying said second catalyst ink on said second electrode backing substrate forming a second catalyst formation;

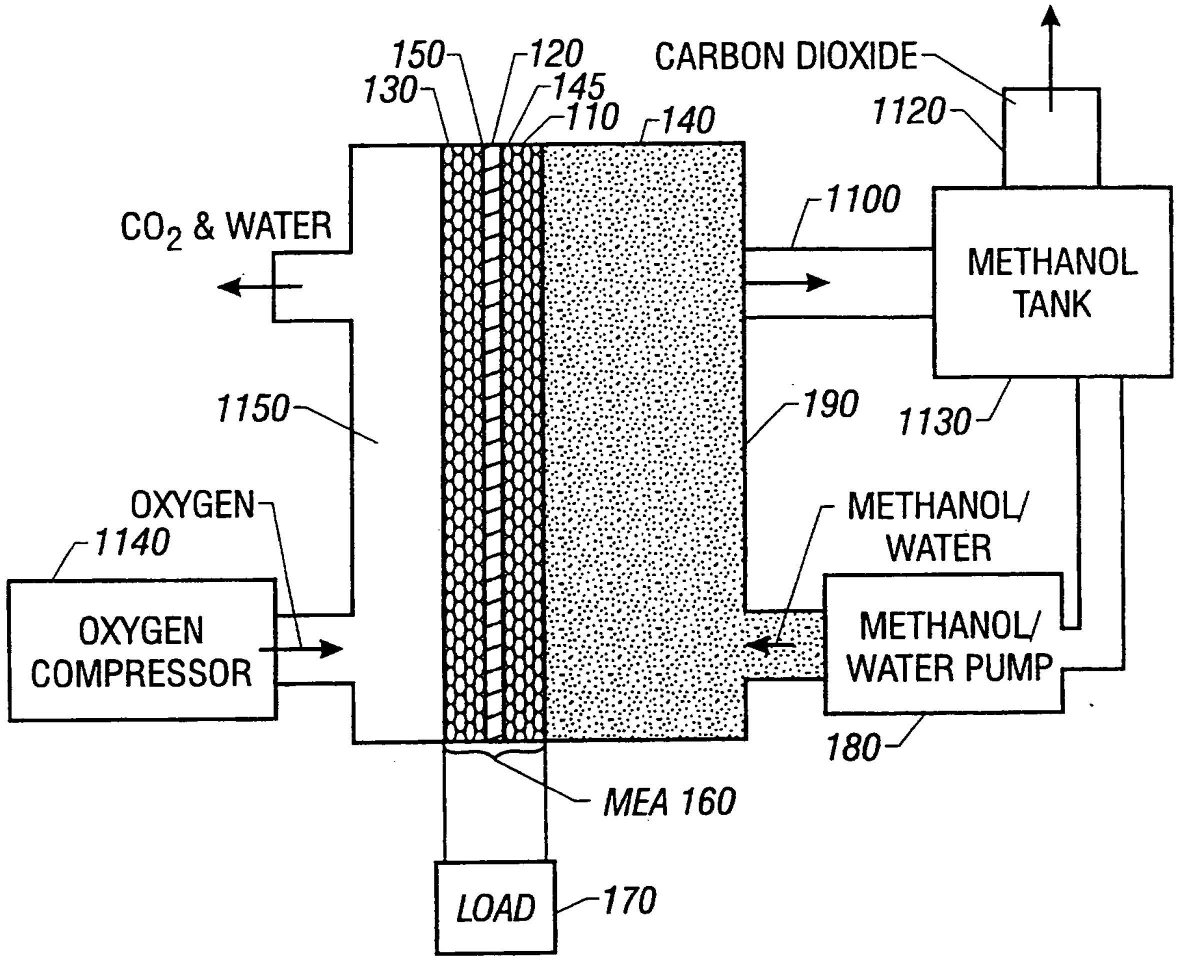
fourth applying said inert pore blocker material on top of said second catalyst formation;

placing said membrane between said first and second electrode backing substrate;

bonding said membrane, said first and second electrode backing substrate to form a membrane electrode assembly.

21. A method as in claim 20, wherein said solid electrolyte membrane is pre-treated with a softening and swelling agent.

22. A method as in claim 21, wherein said softening and swelling agent is an isopropanol solution with a concentration ranging from 10-90% isopropanol.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120
130
145
110
140
CARBON DIOXIDE
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CO_2 & WATER
METHANOL
TANK
1150
190
1130
OXYGEN
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OXYGEN
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METHANOL/
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MEA 160
LOAD
170

FIG. 1

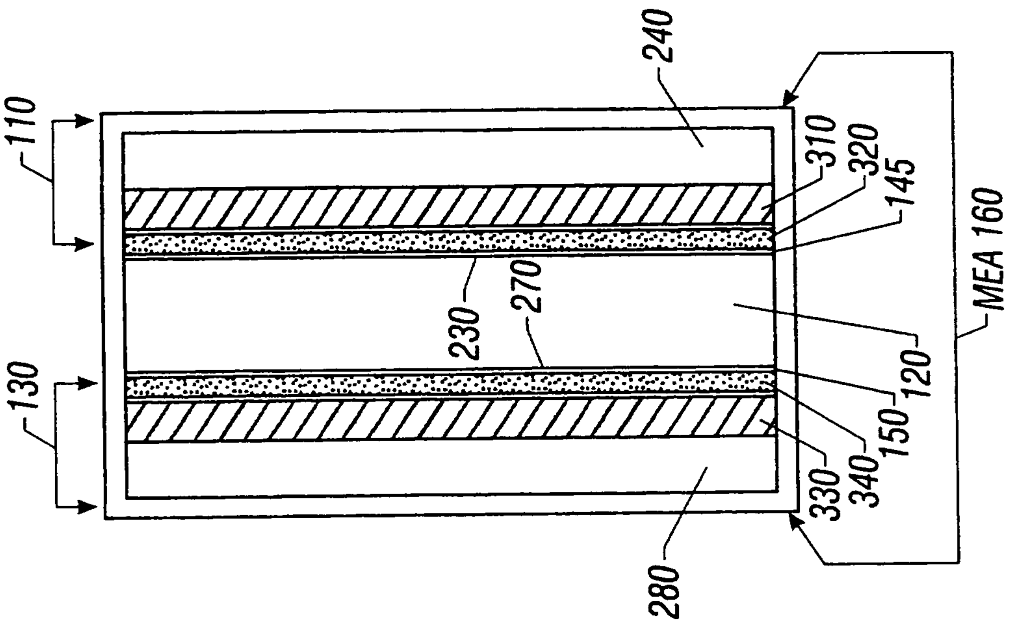
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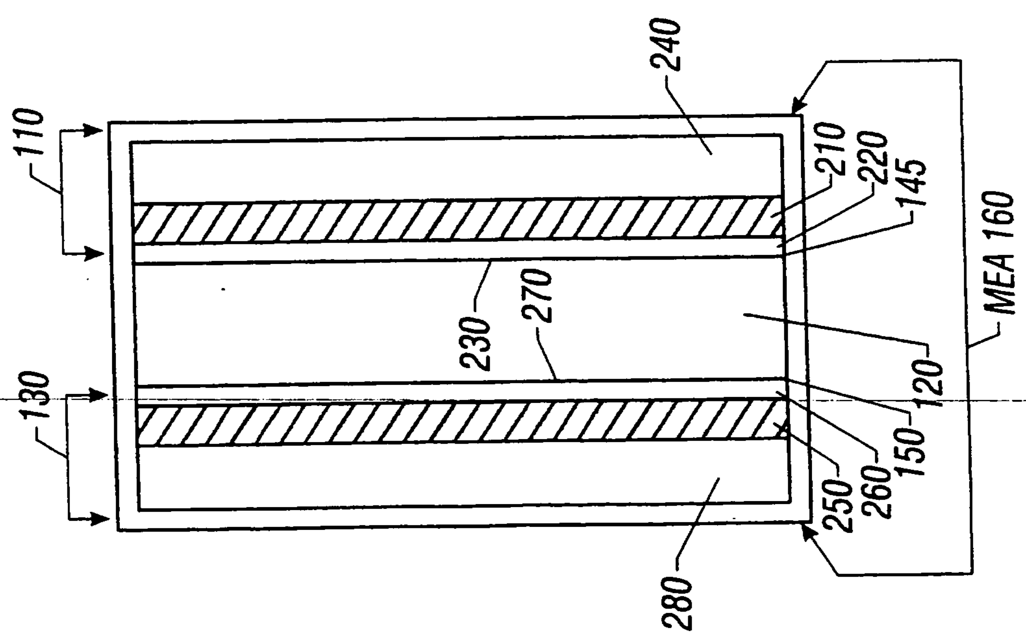
FIG. 3


110
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MEA 160
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FIG. 2